ION-EXCHANGE SEPARATION OF BARIUM IONS AND OTHER ALKALINE EARTH METAL IONS BY DIHYDROGEN TETRATITANATE HYDRATE FIBERS AT 298 K

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Abstract - An ion exchanger, composed of dihydrogen tetratitanate hydrate fibers, $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$, was prepared by synthesizing $\text{K}_2\text{Ti}_4\text{O}_9$ and converting it to a H^+ form. Ion-exchange equilibria of alkaline earth metal ions on the crystalline fibers were measured at 298 K. The ion-exchange reaction is explained in terms of two hydrogen-ions from the fibers being ion exchanged with one alkaline earth metal ion in the aqueous solution. The separation factors were determined for the combinations of barium(II) and other alkaline earth metal ions. The effluent curves for such combinations suggest a successful separation of these metal ions in the aqueous solution.

Key words alkaline earth metal ions, ion-exchange separation, titanate fibers

Ion-exchange separation of alkaline earth metal ions has been reported by several authors using different ion exchangers.[1-3] It has commonly been pointed out in those papers that the ion-exchange efficiency is better for metal ions of larger ionic radii. This is explained by the fact that metal ions which have larger ionic radii are more weakly hydrated. Consequently the larger metal ion is attracted by the ion exchanger more strongly.

Dihydrogen tetratitanate hydrate fiber has been found to be a useful adsorbent for metal ions in aqueous solutions by the authors.[4] Using these fibers, the ion-exchange behavior of alkali metal ions and alkaline earth metal ions are in weakly acidic solutions at 298 K[5-6] has also been studied. Barium(II) ions were much more ion exchanged than the other alkaline earth metal ions, such as strontium(II), calcium(II), and magnesium(II).

In the present study, the separation of barium(II) ions from the other three kinds of alkaline earth metal ions was made as an example of the application of the fibers, arranged in a column, for use as an ion exchanger.

EXPERIMENTAL

Reagents Titanium dioxide used was of 99.9 % purity. All the other reagents were of analytical grade. Distilled and deionized water was used throughout the experiments. The aqueous standard solutions of alkaline earth metal ions, Ba(II), Sr(II), Ca(II), and Mg(II), were prepared by dissolving corresponding chloride salts in water.

Preparation of Layered Dihydrogen Tetratitanate Hydrate Fibers Layered potassium tetratitanate fibers, $\text{K}_2\text{Ti}_4\text{O}_9$, were first synthesized by slow cooling of a K_2MoO_4 flux melt containing K_2CO_3 and TiO_2 (1:3 in molar ratio). After melting the mixtures at 1423 K, the melted materials were cooled to 1223 K (cooling rate: 4K / h), and fibrous crystals of $\text{K}_2\text{Ti}_4\text{O}_9$ were obtained. The fibers were 1 mm in length and 0.01 mm in diameter on average. About a 15 g portion of the fibers was filled in a glass column with an inner diameter of 25 mm. The fibers were washed with 20 dm^3 of water to remove residual K_2MoO_4 . Subsequently, 1 mol dm^{-3} hydrochloric acid was passed through the column to convert $\text{K}_2\text{Ti}_4\text{O}_9$ into a H^+ form according to the following reaction (flow rate: 1 dm^3 / day):

After the potassium-ion concentration in the effluent became less than 1×10^{-5} mol dm^{-3} the fibers were washed with water until the pH value in the effluent was below 5.5 (flow rate: 1 dm^3 /day). The solid product was stocked in a constant humidity box controlled by a saturated NaCl solution (relative humidity: 70 %) to keep the original amount of the

interlayer water in the fibers.

Distribution Studies of alkaline earth metal ions Adsorption experiments of alkaline earth metal ions on the layered dihydrogen tetratitanate hydrate fibers were carried out in batchwise operation at 298 K in a thermostated room. Stoppered glass tubes (20 cm³) were used to equilibrate the solid (0.1 g) with the aqueous solution (10 cm³) containing each alkaline earth metal ion. The initial concentration of each alkaline earth metal ion was 1×10^{-4} mol dm⁻³, and the pH value was adjusted with weakly hydrochloric acid solution. The glass tubes were shaken gently by hand once a day. Fifteen days were required to reach the equilibria of the reactions. After standing the tubes without disturbance for one day, the fibers were separated by aid of centrifugation for 10 min at 4000 rpm. The supernatant solution was analyzed for the metal ions by an atomic absorption spectrophotometer or inductively coupled plasma spectrophotometer. The amounts of metal ions were determined from the difference in the concentrations of the sample and the reference. The distribution coefficient, K_d , was calculated as:

$$K_d = \frac{C_1/g}{C_2/\text{cm}^3} \quad (2)$$

where C_1 is the amount of each alkaline earth metal ion adsorbed per 1 g of the solid, and C_2 is the concentration of each alkaline earth metal ion per 1 cm³ of the aqueous solution.

Separation study of barium and other alkaline earth metal ions The separation of barium(II) ions from mixed solutions of barium(II) and an other alkaline earth metal ion were made as follows: the end of a glass tube (diameter, 10 mm) was filled by usual glass wool. Then 2.5 g of the crystalline dihydrogen tetratitanate hydrate fibers were dispersed in water and poured into the tube. The height of the fibers in the tube was about 15 cm after coming out the water through the glass wool. The column was then washed with large quantities of water. Five-cm³ of barium hydroxide (1×10^{-3} mol dm⁻³) and 5 cm³ of an other alkaline earth metal hydroxide (1×10^{-3} mol dm⁻³) were added to the column. The flow rate was kept at 0.25 cm³/min by using a micro tube pump and 5 cm³ each of the effluent was collected by a mechanical fraction collector. After 150 cm³ of hydrochloric acid solution (1×10^{-3} mol dm⁻³) was passed through the column, the elution was followed with 1 mol dm⁻³ hydrochloric acid solution. The metal content in each fraction was determined by an atomic absorption method or ICP method.

Apparatus A Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrophotometer and Daini Seikosha Inductively Coupled Plasma Spectrophotometer, SPS 1100 were used to determine the concentration of each alkaline earth metal ion in the effluent after the ion-exchange reaction. A EYELA microtube pump was used to control the flow speed in the column and ATTO mini collector were used to obtain the fraction. The pH of the solution was measured with a TOA HM-60S pH meter.

RESULTS AND DISCUSSION

In order to achieve the ion-exchange equilibria of alkaline earth metal ions, a somewhat longer period was necessary than that for the alkali metal ions studied previously[6].

Fig. 1 The ion-exchanged alkaline earth metal ions on the fibers in percent as a function of contact time. Ba(II): ● Sr(II): ◆ Ca(II): ▲ Mg(II): ■ Those values for cesium(I) ions (○) are also plotted as a reference.

In Fig. 1 the values of ion-exchange between the fibers and aqueous solution, are given in percent for alkaline earth metal ions as a function of the contact time. Those values of cesium(I) ions are also plotted as a reference. The equilibration of the ion-exchange reactions needs 15 days for those metal ions. Thus, the ion-exchange experiments were carried out by a batchwise method and were done for 15 days to obtain the equilibrium values.

For the ion separation, it is necessary to know the adequate pH of the elution containing two metal ions. It can, however, be easily obtained from the previous report[6], in which the distribution coefficients, the $\log K_d$, between the fibers and aqueous solution containing alkaline earth metal ions were reported as a function of pH.

TABLE 1 Values of adsorption percent for alkaline earth metal ions on dihydrogen tetratitanate hydrate fibers at pH 2.8 and 0.

	Ba	Sr	Ca	Mg
adsorption(%) (pH 2.8)	97.3	16.7	3.85	0.0570
adsorption(%) (pH 0)	> 0.01	>0.0001	>0.0001	>0.0000001

Fig. 2 The effluent curves of (a) Ba(II)-Mg(II), (b) Ba(II)-Ca(II), and (c) Ba(II)-Sr(II) by column method.

Ion-exchanger: $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$

Column: diameter 10 mm, height 18 cm.

Effluent: alkaline earth metal hydroxide solution; 5×10^{-6} mol

Flow rate: $0.25 \text{ cm}^3 / \text{min}$.

The values of the ion-exchange in percent were calculated using the data in Ref. 6, and adequate pH values for metal-ion separation were determined to be pH 2.8 and 0 (Table 1). The table shows that almost all barium(II) ions will be captured by the fibers but not the other three alkaline earth metal ions, Sr(II), Ca(II), Mg(II). To check this, ion-exchange separations of barium(II) ions from the other three alkaline earth metal ions were performed as described below.

The effluent curves of barium-magnesium(Fig. 2a), barium-calcium(Fig. 2b), and barium-strontium(Fig. 2c) in Fig. 2 were obtained by the column method described previously when using hydrochloric acid solution. The sharp effluent peaks between Ba(II) and other alkaline earth metal ions indicate the almost complete separation. By the first elution with dilute HCl solution (150 cm³ of 1.6×10^{-3} mol dm⁻³), 99.7 % of Mg(II), 99.3 % of Ca(II) and 96.0 % of Sr(II) were successfully recovered. The small amounts of remaining metal ions and Ba(II) ions were completely recovered by the second elution with the HCl solution of 1.0 mol dm⁻³. The results shown in Fig. 2 demonstrate clearly that the dihydrogen tetratitanate hydrate fibers, H₂Ti₄O₉·nH₂O, are applicable for the separation of barium(II) from other alkaline earth metal ions by the column method.

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